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Photochemical reaction of $W(CO)_6$ with $SnCl_4$

II. Synthesis and X-ray structure of tetrachlorobis(triphenylphosphine oxide)tungsten(IV), $[WCl_4(OPPh_3)_2]$

Teresa Szymańska-Buzar *, Tadeusz Głowiak

Institute of Chemistry, University of Wrocław, 50-383 Wrocłow, Poland

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Abstract

The crystal structure of $[WCl_4(OPPh_3)_2]$ (**1**), formed in the photochemical reaction of $W(CO)_6$ with $SnCl_4$ in the presence of triphenylphosphine, has been determined by the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic space group $C2/c$, with $a = 14.027(3)$, $b = 13.163(3)$, $c = 19.621(4)$ Å, $\beta = 96.36(3)°$, $Z = 4$. The structure solved by heavy-atom methods has been refined to $R = 0.0466$, for 3489 observed reflections.

The $[WCl_4(OPPh_3)_2]$ molecule possesses a crystallographically imposed C_2 axis passing through the tungsten atom.

Despite steric demands, a mutually *cis* arrangement of triphenylphosphine oxide oxygens is found for $[WCl_4(OPPh_3)_2]$, while there is a slight lengthening of the W–Cl bonds *trans* to the oxygen atoms.

Keywords: Tungsten(IV); Crystal structure; Triphenylphosphine oxide; X-ray diffraction; Tin

1. Introduction

The Group 6 metal carbonyls are some of the most interesting of the transition metal complexes, in part because of the catalytic properties of these compounds in various chemical processes [1]. In continuation of our research of the catalytic activity of the Group 6 metal carbonyls in the presence of Lewis acids, we have investigated the photochemical reaction of $W(CO)_6$ with $SnCl_4$. Our work has led to the discovery and structural characterization of a new dinuclear tungsten(II) compound, $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ [2]. This compound provides an excellent starting material for compounds of the form $[WCl(SnCl_3)(CO)_3L_2]$ and $[WCl_2(CO)_3L_2]$, with L = acetonitrile, phosphine, bipyridyne, etc. [3]. During attempts to prepare $[WCl(SnCl_3)(CO)_3(PPh_3)_2]$ in the photochemical reaction of $W(CO)_6$ with $SnCl_4$ in the presence of PPh_3 [3], a compound of tungsten(IV), $[WCl_4(OPPh_3)_2]$, was discovered accidentally.

Although a number of tungsten(IV) and molybdenum(IV) complexes of the type $[MCl_4L_2]$ (M = W or Mo; L = RCN [4], py [5–7], phosphines [4,5,7–14] and sulfides [14]) are known, the only notice of the successful synthesis of an M^{IV} complex $MCl_4(OPPh_3)_2$ starting with $MCl_4(RCN)_2$ molecules has appeared [4]; however, no exact information is available.

There are no structural data on phosphine oxide halo complexes of tungsten(IV) or molybdenum(IV), although some examples of W^{VI} and W^{V} oxo halo complexes containing the $OPPh_3$ ligand are known [15–18]. The reason is probably that MCl_4L_2 is readily oxidized to oxo complexes.

2. Results and discussion

2.1. Synthesis of $[WCl_4(OPPh_3)_2]$(1)

The photochemical reaction of $W(CO)_6$ with $SnCl_4$ and PPh_3 in cyclohexane solution following the experimental details [3] gave the tungsten(II) compounds $[WCl(SnCl_3)(CO)_3(PPh_3)_2]$ and $[WCl_2(CO)_3(PPh_3)_2]$ and a small amount of $[WCl_4(OPPh_3)_2]$(**1**). From this

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* Corresponding author.

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mixture of compounds, only the last was obtained in crystalline form.

The reaction mechanism for the formation of compound **1** is not known. However, of the reaction which occurred, there are precedents for the formation of $OPPh_3$ complexes $[MOX_3(OPPh_3)_2]$ and $[MO_2X_2(OPPh_3)_2]$, where M = Mo or W, X = Cl or Br, from the action of halogens on the phosphine-substituted Group 6 metal carbonyls [15]. Tungsten(IV) complexes are formed as products of the oxidation of seven-coordinated tungsten(II) complexes, which appear in the first step of the reaction [2,3]. A similar sequence of reactions with the formation of $WCl_4(PMe_2Ph)_2]$ was observed by Moss and Shaw [10].

It is not obvious as to how the phosphine oxide is formed. The one explanation is that triphenylphosphine can be chlorinated to form Ph_3PCl_2, and on exposure to moist air this can rapidly hydrolyze to triphenylphosphine oxide with the evolution of hydrogen chloride. Displacement of PPh_3 in $[WCl_4(PPh_3)]$ by $OPPh_3$ can then lead to the formation of $[WCl_4(OPPh_3)_2]$.

2.2. Structure of $[WCl_4(OPPh_3)_2]$(1)

Table 1 gives a summary of the crystal data and refinement results obtained for $[WCl_4(OPPh_3)_2]$. Positional parameters and equivalent isotropic thermal parameters are given in Table 2 and 2a. Table 3 gives selected bond distances and bond angles for this compound. The anisotropic displacement parameters for non-hydrogen atoms are listed in Table 4 and these, together with the coordinates and isotropic temperature factors for H atoms, were fixed and have been deposited.

The structure of a single molecule including all non-hydrogen atoms is shown in Fig. 1, which also indicates the atom-numbering scheme used. It can be

Table 1
Crystal data and details of refinement

Chemical formula	$C_{36}H_{30}Cl_4O_2P_2W$
Molecular weight	882.19
Crystal system	monoclinic
Space group	$C2/c$
Cell constants	
a (Å)	14.027(3)
b (Å)	13.163(3)
c (Å)	19.621(4)
β (°)	96.36(3)
V (Å^3)	3600.5(13)
Z	4
T (K)	293(2)
$F(000)$	1736
D_c (mg m^{-3})	1.627
Radiation λ (Mo Kα) (Å)	0.71069
μ (cm^{-1})	3.625
Crystal size (mm)	0.22×0.25×0.25
Method of collection	$\omega/2\Theta$ scan
Refls. determining lattice	25
2Θ range (°)	$20.0 < 2\Theta < 28.0$
2Θ limit (°)	4.0–65.0
Number of reflections	
collected	6234
observed, $I \geq 4.0\sigma(I)$	3489
Residuals R_1, wR_2	0.0466, 0.1257
Final ($\Delta\rho$) (e Å^{-3})	−0.841/0.892

Table 2
Final atomic coordinates with esd's (×10^5) for W, (×10^4) for remaining atoms, and equivalent isotropic thermal parameters with esd's (Å^2 ×10^4) for W, (×10^3) for remaining atoms

Atom	x	y	z	U_{eq} [a]
W	0	36127(3)	25000	367(1)
Cl(1)	1605(1)	3469(1)	3041(1)	26(1)
Cl(2)	482(1)	4885(1)	1730(1)	36(1)
P	224(1)	1714(1)	1258(1)	15(1)
O	364(1)	2452(1)	1852(1)	22(1)
C(11)	−344(1)	566(1)	1500(1)	21(1)
C(12)	−1242(1)	643(1)	1749(1)	34(1)
C(13)	−1734(1)	−226(1)	1915(1)	46(1)
C(14)	−1368(1)	−1145(1)	1818(1)	62(1)
C(15)	−469(1)	−1248(1)	1550(1)	63(1)
C(16)	44(1)	−396(1)	1414(1)	42(1)
C(21)	−491(1)	2202(1)	515(1)	21(1)
C(22)	−1136(1)	1575(1)	119(1)	34(1)
C(23)	−1638(1)	1961(1)	−486(1)	51(1)
C(24)	−1492(1)	2953(1)	−676(1)	50(1)
C(25)	−841(1)	3607(1)	−279(1)	52(1)
C(26)	−343(1)	3195(1)	325(1)	39(1)
C(31)	1384(1)	1417(1)	1005(1)	20(1)
C(32)	1536(1)	1255(1)	333(1)	41(1)
C(33)	2467(1)	953(1)	186(1)	57(1)
C(34)	3204(1)	898(1)	688(1)	50(1)
C(35)	3060(1)	1067(1)	1355(1)	47(1)
C(36)	2143(1)	1338(1)	1529(1)	33(1)

[a] $U_{eq} = 1/3[\Sigma_{ij}U_{ij}a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)]$.

Table 2a
H-atom coordinates with esd's (×10^4) and isotropic thermal parameters (Å^2 ×10^3)

	x	y	z	U_{eq}
H(12)	−1511(4)	1280(5)	1805(4)	40
H(13)	−2319(5)	−167(6)	2093(4)	56
H(14)	−1702(8)	−1722(7)	1927(5)	74
H(15)	−230(8)	−1890(6)	1467(6)	76
H(16)	648(6)	−460(5)	1266(4)	51
H(22)	−1234(4)	910(5)	255(3)	40
H(23)	−2065(5)	1550(8)	−757(4)	61
H(24)	−1830(5)	3202(8)	−1076(4)	60
H(25)	−747(6)	4275(7)	−411(4)	63
H(26)	90(5)	3598(6)	598(3)	46
H(32)	1041(5)	1340(6)	−19(4)	50
H(33)	2567(6)	791(8)	−262(5)	68
H(34)	3816(5)	743(7)	578(5)	60
H(35)	3569(5)	1003(6)	1698(5)	56
H(36)	2045(4)	1462(5)	1983(3)	40

seen that despite steric demands, a mutually *cis* arrangement of triphenylphosphine oxide oxygens is found for [$WCl_4(OPPh_3)_2$], while there is a slight lengthening of the W-Cl bonds *trans* to the oxygen atoms.

The molecule is slightly distorted from octahedral geometry, with the oxygens of the triphenylphosphine oxide ligands occupying *cis* positions and two mutually *trans* Cl atoms. Deviation from ideal geometry occurs for the coordination geometry of the chlorine atoms around the tungsten atom. In the asymmetric *cis* form, the Cl atoms repel each other and give the bond angles, Cl(1)^{i}—W—Cl(2) = Cl(1)—W—Cl(2)^{i} = 95.3(5)°, Cl(1)—W—Cl(2) = Cl(1)^{i}—W—Cl(2)^{i} = 91.0(5)° and Cl(2)—W—Cl(2)^{i} = 91.6(1)°. The bond angle for the mutually *trans* chlorine atoms the Cl(1)^{i}—W—Cl(1) = 170.9(7)°. The W—Cl bond distances are shorter for the mutually *trans* chlorines [W—Cl(1) = 2.387(1) Å] than for the *cis* chlorine [W—Cl(2) = 2.402(2) Å] and are comparable to those found in octahedral W^{V} and W^{VI} complexes [$WOCl_3(OPPh_3)_2$] (2.369(4) Å [18]) and [$WO_2Cl_2(OPPh_3)_2$] (2.385(3) Å and 2.366(3) Å [16]). These W—Cl distances are longer than those observed by Aslanov et al. in W^{IV} complex with mutually *trans* phosphines [$WCl_4(PMe_2Ph)_2$] (2.339(3) Å [9]).

The lengthening of the W-Cl bond *trans* to the oxygen atom can be accounted for, at least in part, in the terms of the *trans* influence of the coordinated phosphine oxide, resulting from the p_{π}–d_{π} oxygen–tungsten bonding.

The coordination geometry around the tungsten atom for the oxygen atoms also shows little deviation from a regular octahedral arrangement. The bond angle O—W—O^{i} is 85.9(2)°. All of the O—W—Cl angles are less than 3° from the angles expected for an

Table 3
Selected bond lengths (Å) and angles (°), with esd's in parentheses [a]

Bond distances			
W—O	2.087(3)	C(14)—C(15)	1.426(14)
W—O^{1}	2.087(3)	C(15)—C(16)	1.374(11)
W—Cl(1)^{1}	2.387(1)	C(21)—C(26)	1.381(9)
W—Cl(1)	2.387(1)	C(21)—C(22)	1.395(8)
W—Cl(2)	2.402(2)	C(22)—C(23)	1.407(9)
W—Cl(2)^{1}	2.402(2)	C(23)—C(24)	1.379(14)
P—O	1.514(4)	C(24)—C(25)	1.422(13)
P—C(21)	1.795(5)	C(25)—C(26)	1.416(9)
P—C(11)	1.796(5)	C(31)—C(32)	1.375(8)
P—C(31)	1.796(5)	C(31)—C(36)	1.400(7)
C(11)—C(16)	1.396(9)	C(32)—C(33)	1.424(9)
C(11)—C(12)	1.405(7)	C(33)—C(34)	1.348(13)
C(12)—C(13)	1.393(9)	C(34)—C(35)	1.366(12)
C(13)—C(14)	1.335(13)	C(35)—C(36)	1.413(8)
Bond angles			
O—W—O^{1}	85.9(2)	P—C(11)—C(12)	118.2(4)
O—W—Cl(1)	86.0(1)	C(11)—C(12)—C(13)	120.5(6)
O—W—Cl(1)^{1}	87.4(1)	C(11)—C(16)—C(15)	119.8(7)
O—W—Cl(2)	91.3(1)	C(12)—C(13)—C(14)	120.2(7)
O—W—Cl(2)^{1}	176.8(1)	C(12)—C(11)—C(16)	118.9(5)
O—W—Cl(1)	87.4(1)	C(13)—C(14)—C(15)	120.5(7)
O^{1}—W—Cl(1)^{1}	86.0(1)	C(14)—C(15)—C(16)	119.8(8)
O^{1}—W—Cl(2)	176.8(1)	P—C(21)—C(26)	118.0(4)
O^{1}—W—Cl(2)^{1}	91.3(1)	P—C(21)—C(22)	120.7(5)
Cl(1)—W—Cl(2)	91.0(5)	C(21)—C(22)—C(23)	119.3(7)
Cl(1)—W—Cl(2)^{1}	95.3(1)	C(21)—C(26)—C(25)	120.8(7)
Cl(1)—W—Cl(1)	170.9(7)	C(22)—C(21)—C(26)	121.2(6)
Cl(1)^{1}—W—Cl(2)	95.3(5)	C(22)—C(23)—C(24)	119.7(7)
Cl(1)^{1}—W—Cl(2)^{1}	91.0(5)	C(23)—C(24)—C(25)	122.0(6)
Cl(2)—W—Cl(2)^{1}	91.6(1)	C(24)—C(25)—C(26)	117.0(8)
W—O—P	156.8(2)	P—C(31)—C(32)	122.7(4)
O—P—C(11)	111.1(2)	P—C(31)—C(36)	116.8(4)
O—P—C(21)	114.2(2)	C(31)—C(32)—C(33)	118.7(7)
O—P—C(31)	107.9(2)	C(31)—C(36)—C(35)	118.7(6)
C(11)—P—C(21)	106.9(3)	C(32)—C(31)—C(36)	120.5(5)
C(11)—P—C(31)	109.4(2)	C(33)—C(34)—C(35)	120.6(6)
C(21)—P—C(31)	107.2(2)	C(34)—C(33)—C(32)	120.9(7)
P—C(11)—C(16)	122.8(4)	C(34)—C(35)—C(36)	120.5(7)

[a] Symmetry code: (i) $-x$, y, $-z+1/2$.

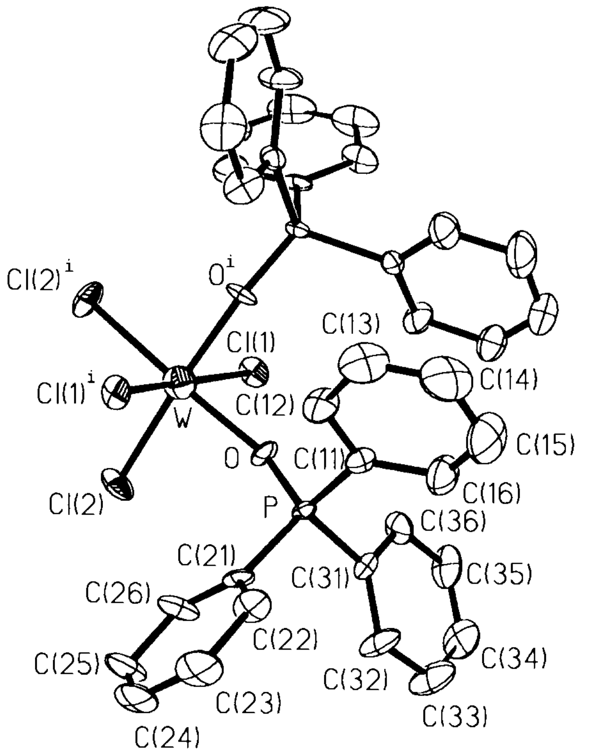

Fig. 1. ORTEP [25] drawing of [$WCl_4(OPPh_3)_2$] showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Atoms related by the C_2 axis of symmetry are denoted by i.

ideal octahedral arrangement, with the exception of O^i —W—Cl(2)^i = 91.3(1)°.

The two *cis* $OPPh_3$ ligands are bonded at the same distances from the metal atom, are unstrained and related by twofold symmetry. The W—O—P angles are 156.8(2)° and are smaller than those found in compounds with mutually *cis* $OPPh_3$ ligands, i.e. [$WOCl_3(OPPh_3)_2$] (159.9(7)° [18]) and [$WO_2Cl_2(OPPh_3)_2$] (159.0(4)° and 165.4(5)° [16]), but close to those in $HPPh_3$ [$WOCl_4(OPPh_3)$] (155.7(11)° [17]) which has only one $OPPh_3$ ligand.

The W-$OPPh_3$ bond lengths are 2.087(3) Å and are comparable to those found in oxo compounds, i.e. $HPPh_3$[$WOCl_4(OPPh_3)$] (2.06(2) Å [17]) and [$WOCl_3(OPPh_3)_2$] (2.088(11) Å [18]); these W-O distances are shorter than those observed by De Wet et al. in the dioxo tungsten(VI) complex [$WO_2Cl_2(OPPh_3)_2$] (W-$OPPh_3$ = 2.175(8) Å and 2.163(7) Å [16]).

The geometry of the $OPPh_3$ ligand shows no unusual features. The P-O bond, 1.46(1) Å in free $OPPh_3$ [19], is only slightly affected by the coordination to WCl_4 in **1** (1.514(4) Å). The phosphorus atoms show tetrahedral coordination, being surrounded by the atoms C(11), C(21), C(31) and O. The tetrahedral angles vary from 106.9(2)° to 114.2(2)°. The P-O bond lengths are the same [1.796(5) Å] and the mean C-C value is 1.39 Å.

Compound **1** is a unique example of an X-ray investigated complex MCl_4L_2 (M = Mo, W; L = N, P, O, S-donor ligands) with a *cis* geometry. A *trans* geometry proposed on the basis of IR, ^1H and ^{31}P NMR spectroscopy for different tertiary phosphines, C_3H_7CN and SC_4H_8 complexes of this type [12,14]. X-ray analysis has confirmed that [$WCl_4(PMe_2Ph)_2$] is *trans* [9].

Table 4
Anisotropic displacement parameters with esd's ($Å^2 \times 10^3$) [a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	33(1)	41(1)	35(1)	0	−1(1)	0
Cl(1)	14(1)	35(1)	28(1)	2(1)	−10(1)	−3(1)
P	13(1)	21(1)	9(1)	−4(1)	1(1)	1(1)
Cl(2)	33(1)	36(1)	39(1)	22(1)	4(1)	−5(1)
O	25(2)	27(2)	14(2)	−13(1)	−1(1)	5(1)
C(11)	21(2)	22(2)	20(3)	−6(2)	4(2)	−6(2)
C(12)	21(2)	37(3)	45(4)	−1(3)	15(2)	−5(2)
C(13)	37(3)	52(4)	53(5)	−6(3)	14(3)	−25(3)
C(14)	82(7)	43(5)	63(6)	0(4)	22(5)	−30(4)
C(15)	79(6)	27(4)	91(8)	−6(4)	34(6)	−9(4)
C(16)	50(4)	5(3)	55(5)	−4(3)	19(3)	0(3)
C(21)	18(2)	38(3)	7(2)	−5(2)	−1(2)	3(2)
C(22)	24(2)	51(4)	23(3)	−8(2)	−10(2)	5(2)
C(23)	38(4)	88(6)	22(4)	−6(4)	−15(3)	16(4)
C(24)	45(4)	87(6)	16(3)	8(3)	−10(3)	22(4)
C(25)	64(5)	72(5)	21(4)	21(4)	1(3)	16(4)
C(26)	50(4)	49(4)	15(3)	10(3)	−2(2)	−6(3)
C(31)	17(2)	20(2)	24(3)	−7(2)	5(2)	1(2)
C(32)	29(3)	66(5)	31(4)	−15(3)	15(2)	5(3)
C(33)	41(4)	83(6)	50(5)	−14(4)	28(4)	6(4)
C(34)	26(3)	62(5)	66(6)	3(4)	21(3)	12(3)
C(35)	20(3)	50(4)	69(5)	2(4)	1(3)	16(3)
C(36)	21(2)	41(3)	36(3)	9(3)	0(2)	11(2)

[a] Anisotropic vibrational amplitudes in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12} + \ldots)]$

The *cis* structures were assigned only from a study of infrared spectra in the W—Cl stretching region for WCl_4L_2 (L = CH_3CN, C_2H_5CN and $S(C_2H_5)_2$ [14]). Exactly the same arrangement and symmetry about the metal atom as in **1** has only been observed in $[UCl_4(OPPh_3)_2]$ [20].

3. Experimental details

All reaction and manipulation were carried out under N_2 by using Schlenk techniques. The solvents used were dried, distilled and deoxygenated.

The photochemical reaction was carried out in a glass reactor fitted with a quartz window. An HBO 200 mercury lamp was used as the light source.

3.1. Synthesis of $[WCl_4(OPPh_3)_2]$(1)

We attempted to prepare $[WCl(SnCl_3)(CO)_3(PPh_3)_2]$ from the photochemical reaction between $W(CO)_6$, $SnCl_4$ and PPh_3 following published experimental details [15]. However, we obtained this compound as a mixture with $[WCl_2(CO)_3(PPh_3)_2]$ and $[WCl_4(OPPh_3)_2]$, from which $[WCl(SnCl_3)(CO)_3(PPh_3)_2]$ and $[WCl_4(OPPh_3)_2]$ were separated by extraction with toluene. The solvent was removed in vacuo leaving an orange solid, which was then washed with cyclohexane and pumped dry. The solid was crystallized from a mixture of dichloromethane, toluene and heptane yielding $[WCl(SnCl_3)(CO)_3(PPh_3)_2]$ as an orange powder and dark orange crystals of $[WCl_4(OPPh_3)_2]$, which were used for the X-ray structure determination.

3.2. Crystal structure analysis of $[WCl_4(OPPh_3)_2]$(1)

Crystals of **1** were grown from CH_2Cl_2/toluene/heptane (−10°C). The single crystals used for the X-ray examination were removed from the flask, rapidly coated with a light hydrocarbon oil to protect them from the atmosphere and sealed in a capillary.

Crystallographic data were obtained using a KM4 κ-axis computer-controlled [21] four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Details of the crystal data intensity measurements are given in Table 1. No absorption or extinction corrections were applied. The 3489 unique data with $I \geq 4.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $C2/c$.

The structure was solved by heavy-atom methods with the SHELXS-86 program [22] and refined by a full-matrix least-squares method, using the SHELXL program [23]. For non-hydrogen atoms, refinement with anisotropic temperature factors converged to $R_1 = 0.0466$ and $wR_2 = 0.1257$. The final atomic positions are given in Table 2. Coordinates and isotropic temperature factors for H atoms were fixed and together with thermal motion parameters have been deposited with the Cambridge Crystallographic Data Centre. Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography* [24].

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